

FUSED SALTS, CONTAINING
WATER OF CRYSTALLIZATION,
AS SOLVENTS

BY
H. K. BENSON, A.M.

DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY
OF PURE SCIENCE OF COLUMBIA UNIVERSITY

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H. K. B.

I. OBJECT OF THE INVESTIGATION.

The depression of the freezing point of a solvent by the addition to it of a soluble substance has been in use now for a number of years as a means of determining the molecular weight of the dissolved substance. Almost all kinds of liquids have been employed as solvent for this purpose, but so far as can be ascertained no one has used salts which contain water of crystallization.¹ These salts melt to form a clear liquid at comparatively low temperature and fulfil the condition necessary for the method, *i. e.*, on cooling, even in the presence of a second substance, they separate a solid having the same composition as the liquid solvent. Though the original and primary object of this investigation was the study of such solvents for freezing point purposes, later work on the coefficients of partition of substances between such solvents and other, immiscible ones has led to results which apparently will do much toward clearing up the abnormalities encountered in the freezing points, boiling points, vapor pressures, and osmotic pressures of concentrated solutions in all solvents. In other words, the results of the investigation are far more general than was at first expected, or are shown by the title. The results of the work on distribution and their discussion form the second part of this paper.

II. APPARATUS.

The freezing point apparatus used was the form designed by Smeaton. It consists of an outer insulated vessel filled with a suitable refrigerating agent, next an air chamber, then an inner receptacle for refrigeration in which is placed the air bath which holds the tube containing the solution. Both the stirrer in the refrigerating agent and the one in the solution are driven by a small electric motor to insure uniformity of temperature.

In making the determinations, a normal certified thermometer reading $2/_{100}^{\circ}$ (G. S. No. 5853, 1903) was used. The sur-

¹ When this research was practically finished, as far as concerns the freezing point, it was discovered that Löwenherz (*Zeit. f. phys. Chem.*, 18, 70, 1895) had used $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in a similar way, but more to fix the composition of the $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ than to determine the molecular weights of the dissolved substances.

rounding bath was kept from 4° – 8° below the freezing point of pure solvent. A weighed amount of the fused salt was introduced into the tube, a weighed amount of substance then added and the resulting solution slightly supercooled. A small crystal of the pure solvent was then added, the internal stirrer set to work and the highest point on the thermometer read. The overcooling was kept, whenever possible, within 1° . Each determination was repeated at least twice and checked within 0.02° . In all cases where the overcooling exceeded 1° , correction was made for the increased concentration by means of the formula $f = \Delta t \frac{c}{w}$, where f is the fraction of liquid separating as solid, c , the specific heat of the solvent, w , its latent heat of fusion and Δt , the number of degrees of overcooling. In every case it was ascertained by analysis that the solid separated had the composition of the pure solvent.

III. PREPARATION OF THE SOLVENTS.

$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.

The hexahydrate of calcium chloride melts in its own water of crystallization at 29.48°C . The pure salt was melted by placing the bottle containing it in warm water. During the melting the mouth of the bottle was protected from moisture by absorbent cotton. After melting, the bottle was placed in cold water, the liquid mass supercooled, infected with a crystal of the hexahydrate and the resulting solidified mass drained of its adherent liquid. This process was repeated until the liquid showed a constant freezing point. The solid was then remelted and employed as solvent.

In order to obtain the value of the molecular depression of the freezing point, use was made of the relation derived from

thermodynamical considerations, $K = \frac{.02T^2}{w}$, where w is the latent heat of solidification for 1 gram of solvent and T the freezing point of the pure solvent. According to Person,¹ the latent heat of solidification for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ at its freezing point is 40.7 cal., hence $K = \frac{(273^{\circ} + 29.48)^2 \times .02}{40.7} = 45$.

¹ See Tammann, *Kristallisieren und Schmelzen*, p. 45.

$$\text{LiNO}_3 \cdot 3\text{H}_2\text{O}.$$

The crystallized salt, lithium nitrate, was used as the starting point for the preparation of the solvent. The bottle of the salt was placed in water at 40° C. and small quantities of distilled water added from time to time until complete solution was obtained. The resulting liquid was then supercooled, infected with a small crystal of the trihydrate of lithium nitrate and the needle-shaped crystals drained from the excess of solution. Several crystallizations thus made yielded a salt with a constant melting point of 29°.88 C. No value of the latent heat of fusion being available for the calculation of the molecular constant, K , it was determined experimentally as shown below:

Substance.	Gms. per 100 gms. solvent.	Δ .	K .
Glycol	2.101	0.880	25.9
KNO_3	2.037	0.520	25.8
LiBr_2	2.570	0.780	26.4

Average 26.0

The value of w , the heat of fusion of 1 gram of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ calculated from this, *i. e.*, $w = \frac{.02T^2}{K} = \frac{.02 \times (273 + 29.88)^2}{26}$, is 70.6 cal.

$$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}.$$

For the preparation of the decahydrate of sodium chromate, the Eimer and Amend salt was used. The minimum amount of water necessary to dissolve the salt was added. The solution thus obtained was supercooled, infected with a crystal of the decahydrate and the crystals formed were hurriedly drained of adherent liquid by suction.

The crystals thus obtained were bright yellow plates, belonging to the monoclinic system. They melt in their own water of crystallization at 19°.92 c. The molecular constant used in the measurements with sodium chromate as solvent was obtained in the same manner as the one obtained for lithium nitrate, and its value calculated from solutions of urea in sodium chromate is 38.7, while the constant calculated from the heat of fusion as

determined by Berthelot¹ gives the value of 43.8. The accuracy of the former will be verified by work which is now being done with this solvent.

IV. MOLECULAR WEIGHTS BY FREEZING POINT DEPRESSIONS.

CaCl₂·6H₂O as Solvent.

I. Glycerine² [92].

Grams of substance per 100 grams of solvent.	Δ .	M.
3.160	1°.580	90.0
5.484	2°.740	90.7
6.962	3°.460	90.5
7.864	3°.732	86.5
9.590	4°.911	88.0
13.425	7°.260	83.2

II. Urea³ [60]

0.891	0°.595	67
1.185	1°.185	66
3.860	2°.560	68

III. Glycol⁴ [62]

2.633	1°.640	70
3.300	2°.153	68
5.341	3°.345	72

IV. Potassium chloride⁵ [74]

0.292	0°.181	73
0.702	0°.423	75

V. Calcium bromide⁶ [200]

0.371	0.087	192
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¹ Ann. chim. phys. [5], 15, 215, 242, 1878.

² Kahlbaum's "Special K".

³ Kahlbaum's c. p. unpurified.

⁴ Museum specimen of ethylene glycol.

⁵ Kahlbaum's, recrystallized three times.

⁶ Prepared from Iceland spar and pure hydrobromic acid. In concentrated solutions the freezing point is increased, due possibly to the formation and separation of the solid $\text{CaBr}_2 \cdot 6\text{H}_2\text{O}$.

VI. Hydrochloric acid¹ [36.5]

Grams of substance in 100 grams of solvent.	Δ .	M.
0.347	0°.421	37
0.438	0°.605	33
0.861	1°.181	33

VII. Potassium nitrate² [101].

0.596	0°.520	51
1.513	1°.198	56
1.564	1°.180	58

VIII. Ethyl alcohol³ [46].

0.2652	0°.21	57
1.0958	0°.89	56
1.8550	1°.32	63
3.5057	2°.21	71
4.2900	2°.47	78
5.2140	2°.85	82
7.2292	3°.40	96
9.2517	3°.83	109
11.4259	4°.26	121
13.5912	4°.68	131
19.6313	5°.57	158
25.2080	6°.47	175

IX. Acetic acid⁴ [60].

1.041	0°.63	74
1.388	0°.84	74
1.975	1°.20	75
2.878	1°.46	92
13.034	4°.99	121
16.440	5°.74	131
22.180	6°.68	150
33.680	8°.67	174

¹ The pure dry HCl gas was passed directly into the tube containing the solvent and the concentration determined by titration after the freezing point had been observed.

² *Kahlbaum's*, not further purified.

³ *Kahlbaum's* absolute.

⁴ *Kahlbaum's* "Special K",

X. Formic acid¹ [46].

Grams of substance per 100 grams of solvent.	Δ .	M.
1.146	1° .00	51.7
5.288	4° .11	58.0
8.647	6° .12	63.7
8.844	6° .18	64.0
14.775	9° .58	69.0

XI. Equimolecular mixture of formic and acetic acids.

1.293	1° .00	59
1.861	1° .36	64
4.888	3° .16	71
10.810	5° .92	84
15.540	7° .62	92

These results, which are plotted in a curve, indicate that neither the formic acid nor the acetic acid has any effect upon the other; in other words the effect of each is the same in this mixture as when it is present alone.

*LiNO₃.H₂O as Solvent.*²

XII. Glycol [62].

Grams of substance in 100 grams of solvent.	Δ .	M.
2.101	0° .880	62
3.553	1° .500	61
4.153	1° .811	59
6.107	2° .620	60
22.120	9° .880	58

XIII. Erythrite [122].

1.102	0° .261	110
2.350	0° .640	95
3.610	0° .963	98
3.983	1° .020	101
7.007	1° .821	100

¹ Kahlbaum's "Special K."

² The substances used here were identical with those used in CaCl₂. 6H₂O. The mannite and erythrite used here gave in water the following results by the freezing-point method:

	Grams per 100 grams H ₂ O.	Δ .	M.
Mannite [182]	1.532	0° .160	178
Erythrite [122]	5.000	0° .765	121

XIV. Acetone¹ [58].

Grams of substance in 100 grams of solvent.	Δ .	m.
0.898	0°.400	58.3
3.644	1°.511	62.7
4.075	1°.642	64.6
8.020	2°.870	72.6

XV. Mannite [182].

0.412	0°.062	174
1.529	0°.220	180
1.842	0°.281	171
3.011	0°.450	174

XVI. Methyl alcohol [32].

0.939	0°.781	31
3.277	2°.550	33
5.819	4°.230	35
7.023	4°.810	37
13.825	8°.730	43

XVII. Ethyl alcohol [46].

1.953	1°.040	48
5.356	2°.461	56
8.704	3°.320	68
9.040	3°.500	67
17.136	5°.042	88

XVIII. Acetic acid [60].

2.700	1°.160	60
4.310	1°.791	62
5.631	2°.262	62
8.486	3°.118	70
8.974	3°.180	73

XIX. LiBr₂ [87].

1.492	0°.441	88
1.585	0°.480	86
2.570	0°.782	86

¹ Kahlbaum's, not further purified.² From specially prepared LiCO₃ and HBr.

XX. KNO_3 [101].

Grams of substance in 100 grams of solvent,	Δ ,	M.
1.262	$0^\circ.318$	102
1.717	$0^\circ.440$	101
2.037	$0^\circ.521$	101

XXI. KCl [74].

0.304	$0^\circ.200$	39
3.545	$2^\circ.760$	33

XXII. HCl [36.5].

0.321	$0^\circ.48$	18.5
0.642	$1^\circ.00$	17.7

XXIII. LiCl^1 [42].

0.7864	$0^\circ.50$	41
1.3487	$0^\circ.88$	40

XXIV. CdCl_2^2 [183].

430	$0^\circ.071$	158
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$\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ as Solvent.³

XXV. Urea [60].

0.670	$0^\circ.434$	59
1.340	$0^\circ.841$	61
2.017	$1^\circ.192$	65

XXVI. Glycol [62].

0.7360	$0^\circ.434$	65
1.9577	$1^\circ.078$	70
6.7100	$3^\circ.640$	70

XXVII. Glycerine [92].

1.672	$0^\circ.720$	90
4.541	$1^\circ.891$	93
10.736	$4^\circ.370$	95

¹ Specially prepared LiCO_3 and HCl .

² *Kahlbaum's*, not further purified.

³ The measurements with $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ as solvent were made in collaboration with Mr. J. S. Mills, who is at the present time extending this work in this laboratory, and will be reported upon later.

XXVIII. NaNO_3 [85].

Grams of substance in 100 grams of solvent.	Δ .	M.
0.9016	0°.408	86.

XXIX. NaCl [58].

1.006	0°.622	62.
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V. PECULIAR RESULTS FOR WATER. EFFECT OF INFECTION OF
OVERCOOLED $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ WITH A CRYSTAL OF
 $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

Water, by the regular method, for all three solvents, gave abnormal results which ran from 198 for small amounts of water to 79 for comparatively large amounts (20 grams per 100). In none of these cases could any abnormality in the composition of the separated solid be observed by analysis and since no conclusion can be drawn from, the results will not be given until investigated further.

By the Richards' method¹ in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ the following results were obtained.

XXX. H_2O [18].

Grams per 100 grams of solvent.	Δ .	M.
3.8	0°.82	24.2
4.4	0°.82	17.3
8.0	2°.32	20.9

Higher concentrations than these could not be used owing to the fact that the solid solvent, previously formed, dissolved in the water added, even though the temperature of the latter was low, and the temperature rose above the freezing point of the solvent.

When the overcooled pure solvent, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, is infected not with a crystal of the hexahydrate, but with one of the dihydrate,

¹ *Jour. Am. Chem. Soc.*, **25**, 291 (1903). Using a mixture of solid $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in presence of its pure liquid phase and finding the depression of the freezing point after the addition of varying amounts of water,

$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, a solid is separated at a lower point ($26^\circ.80$) than after infection with the hexahydrate, and the later addition of a crystal of the hexahydrate caused the solution already infected with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ to rise to the normal freezing point, viz., $29^\circ.48$. This would indicate, contrary to the conclusion of Roozeboom¹ that $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ can exist as a solid, in presence of solution, below $60^\circ \text{C}.$ ² for the solid in this case, by analysis, showed that composition.

VI. DISCUSSION OF FREEZING POINT RESULTS.

It will be seen from the foregoing results that fused salts, which contain water of crystallization when employed as solvents for freezing point purposes, behave very much as water does, except that they reduce or drive back completely the ionization of dissolved salts, when these have an ion in common. The molecular weights of many other substances seem to be the same as in water.

As is well-known, abnormal results are found in some concentrated solutions with water and other solvents, and here also we observe ever increasing abnormality with increasing concentration, in the case of the alcohols and formic and acetic acids. Before drawing any conclusions from these it will be necessary to examine the derivation of the freezing point law, in order to ascertain whether these are really abnormalities or simply apparent abnormalities due to a common and mistaken use of the freezing point law.

In the derivation of the van't Hoff-Raoult formula for the relation between the osmotic pressure of a solution and the vapor pressure of the pure solvent, the assumption is made that the heat of dilution is negligible. If this premise is not true of a solution, then (i. e., if the solution, in case there is a heat of solution, is not infinitely dilute) it is hardly correct to assume that results in strong solutions are abnormal, and naturally absurd to attempt to draw conclusions from them.

The attempts which have thus far been made to formulate a relation applying when there is a heat of solution are sum-

¹ *Zeit. f. phys. Chem.*, 4, 31, 1889.

² This point is still under investigation and will be reported upon later.

marized by Bancroft,¹ but a very accurate quantitative relation apparently has not yet been found and experimentally tested even for the cases of osmotic and vapor pressures, though the qualitative effect of the heat of dilution upon these and upon all relations depending upon these is apparently beyond all doubt.

Naturally, if osmotic pressure is affected in this way by the heat of dilution, the depression of the freezing point and the increase of the boiling point must also be affected, for the law governing these can only be derived by aid of a reversible cycle involving osmotic pressure or vapor pressure.

The principle of the depression of the freezing point (and also of the increase of the boiling point) is most simply and readily grasped by a modified form of the method of derivation employed by Macloskie.² Assume we have an infinite amount of aqueous solution containing x moles of dissolved substance in each 100 grams. Assuming that there is no heat of solution, and that the gas laws hold, the osmotic work necessary to separate 100 grams of the pure solvent by aid of a semi-permeable piston will be $x R T$, for it is equivalent to separating x moles from the solvent in which they have been previously dissolved. To separate this same amount of solvent by isothermal crystallization as solid would require the heat $100 \times w$, where w is the latent heat of solidification of 1 gram of solvent. Since by the second law of thermodynamics we have the relation:

$$\frac{\text{Work necessary}}{\text{Heat available to do work}} = \frac{\text{Degrees thro' which heat must fall to do this amount of work}}{\text{Higher absolute temperature'}}$$

the application of our data, expressing the work as heat, leads to the expression

$$\frac{x R T}{100 w} = \frac{\Delta_x}{T}$$

where T is the freezing point of the solvent, and Δ_x the depression of the freezing point due to x moles per 100 grams of solvent, *i. e.*, g/M , where g is the number of grams per 100, and M is the

¹ *Jour. Phys. Chem.*, **10**, 319, 1906. See also Richards and Forbes, *Pub.* 56, Carnegie Institution.

² *Science*, N. S., **9**, 206-207 (1899).

molecular weight. For 1 mole per 100 grams, this becomes the well-known $K = \frac{.02 T^2}{w}$, since $R = 2$ cal, Δ_x becoming K .

In the above derivation we have assumed that no specific heating or cooling results by the concentrating effect of the removal of 100 grams of pure solvent from the solution, *i. e.*, we have neglected to consider the possible heat of concentration. In case heat is absorbed (or evolved) when the solution is thus concentrated, the difference in energy (for the case of x moles in 100 grams) of the solution, before and after the separation, will not be xRT , but $xRT + Q$ or $(xRT - Q)$, for heat must be supplied (or removed) to retain the temperature constant.

A heat of concentration would also affect the denominator, for then heat will be absorbed (or evolved) by the concentration, in addition to that evolved by the separation of solid. The difference of energy, before and after the separation of the 100 grams, then, would not be w , but $100 w - Q$ (or $100 w + Q$), according as heat is absorbed or evolved on concentration. We would have, then, assuming the gas laws to hold in these cases, and, considering the heat of concentration,

$$\frac{T(2xT + Q)}{100 w - Q} = \Delta'_x,$$

where Q is the heat of concentration due to the removal of 100 grams of solvent, which has previously contained x moles from the solution, *i. e.*, the heat involved in thus concentrating this solution. Q is considered positive when heat is evolved when the substance dissolves, and negative when heat is absorbed on solution.

A glance at this formula shows that qualitatively it is thoroughly in accord with the facts. Sulphuric acid leads to a molecular weight of 28.4 in a 2.5 molar solution,¹ (*i. e.*, 24.52 grams per 100, $\Delta = 18.275$) and hydrochloric acid leads to the value 11.4 in a 3 times molar solution (10.95 grams per 100, $\Delta = 18.096$). Even granting complete ionization into three ions in the case of sulphuric acid, the smallest possible molecular weight would be 36; and a complete ionization of the hydrochloric acid would lead as a minimum value of 18.25. In neither case can the ionization be such, and in both cases heat is given out on dilution

¹ Jones and Getman: *Am. Chem. J.*, 27, 436, 1902.

(absorbed on concentration), *i. e.*, we have $\Delta'_x = \frac{T(2xT+Q)}{100w-Q}$, in which Q is positive; and Δ'_x , the corrected value, is very much larger than Δ_x , so that this absurd value for the molecular weight would no longer be obtained.

In case heat is absorbed when the substance dissolves (*i. e.*, is evolved on concentrating), Q has a negative value, and we have

$\Delta'_x = \frac{T(2xT-Q)}{100w+Q}$, *i. e.*, the corrected depression is smaller

than the uncorrected one and the apparent molecular weight is abnormally large. This is illustrated by the case of ethyl alcohol in benzene¹ which according to Walker² dissolves with a marked absorption of heat. The apparent molecular weight in these solutions, increases from 45.9 to 318 for concentrations from 0.164 to 32.45 grams per 100 grams of solvent.³

The cause of the great effect of the heat of dilution or really of concentration, in the freezing point formula is obvious for the sign of Q in the numerator is always contrary to that in the denominator, so that the effect of Q in increasing or decreasing the value of the depression is very greatly intensified.

In the results in fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, given above, it will be seen that for ethyl and methyl alcohol and acetic and formic acids, the apparent molecular weights increase very rapidly with the concentration (*i. e.*, with x), and in accord with the above formula we find heat absorbed on solution; and the more abnormal the result the greater the heat absorbed, for the correction for any one solution depends upon the value of x . This is not only true for varying concentrations of the same substance in the same solvent, but also for the same substance in the two solvents, *viz.*, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$. In other words, the heat absorbed by the solution in forming any one of the concentrations of either alcohol or acetic acid, and consequently, evolved on concentrating, is greater in the case of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ than in $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, and the *apparent* result is more abnormal, for Q is greater in the former case than in the latter.

¹ Beckman: *Zeit. f. phys. Chem.*, 2, 728, 1888.

² *Trans. Roy. Soc., Canada*, 8, III, 105 (1902).

³ Beckman, *Zeit. f. phys. Chem.*, 8, 227, 1891.

It seems quite evident, then, that before we can reason from the results of the freezing point or boiling point in concentrated solutions, or even accept them as indicating anything it is necessary at least to correct the formulas as above, so that the heat of concentration may be brought into them. No attempt has been made to do this quantitatively in this paper, that is a question for the future. It is sufficient here to call attention to the fact that freezing points and boiling points can be treated as vapor pressures and osmotic pressures have already been treated by Bancroft,¹ and that they may lead to satisfying results, without any assumptions, by simply expanding the premises upon which the derivation of the formulas is based, to meet the conditions observed in actual work for concentrated solutions. It is to be remembered, however, that no attempt is made to account for the variation in solution of the gas laws; they are assumed to hold, at least, approximately.

It will be seen from the above resumé that all our methods for the determination of molecular weight, depending upon freezing point, boiling point, vapor pressure and osmotic pressure in strong solutions will only give the real results when corrected for the heat of concentration, and perhaps other things, and the question arises—is there no method for the determination of the molecular weight that is free from this objection, or in which these corrections are unnecessary? In answer to this question it may be said that such a method does exist and that it can be used in connection with any one of the other methods. This method is the well-known one depending upon the coefficient of distribution or partition of a substance between two immiscible solvents. Strange to say, no one seems to have realized that this method is independent of the heat of solution. This may be the consequence of the usual method of its derivation, or it may be due to the fact that no one else has compared its results with those by the other methods. The results of the application of this method to the solutions considered above is the subject of the following sections. It may be said in anticipation, however, that by it some of the abnormally behaving solutions considered above from the point of view of

¹ *Loc. cit.*

freezing point show a constant molecular weight throughout all concentrations and make evident the fact that it is the fault of the other methods, unless corrected as above, that apparently abnormal results for the molecular weight are obtained.

VII. THE COEFFICIENT OF DISTRIBUTION.

According to Nernst¹ and Aulich² and others³ it is possible to find the relation between the molecular weights of a substance in two immiscible solvents by distributing it between them. The simplest derivation⁴ of this is the following, for it brings out most plainly the important point that this distribution, and hence the ratio of the molecular weights found, is unaffected by the heats of solution of the substance in the two solvents.

Assume the formula of the substance to be MA in the one solvent and (MA)_n in the other, where *n* is equal to 1 or greater. The chemical reaction in the two-layer, heterogeneous equilibrium will be then $n\text{MA} = (\text{MA})_n$ and the constant of the law of mass

action, at any one constant temperature, will be $K = \frac{C_{(\text{MA})_n}}{C_{\text{MA}}^n}$;

and this will remain the same, independent of the total amount of substance available for distribution between the two liquids. Here if $n = 1$, and the substance is a gas, one phase being the gaseous, the other being the liquid, saturated with gas, we have

the well-known Henry's law, *i. e.*, $\frac{C_{\text{as gas}}}{C_{\text{in sol.}}} = \text{constant}$. When

$n = 2$, the solvents being water and benzene, the substance benzoic acid, the ratio C_w^2/C_B is constant for any one temperature independent of the total amount of benzoic acid present in the system.⁵

¹ *Zeit. f. phys. Chem.*, **8**, 110, 1891.

² *Ibid.*, **8**, 105, 1891.

³ See Hantzsch and Sebalt, *Zeit. f. phys. Chem.*, **30**, 258, 1899; Hantzsch and Vagt, *ib.*, **38**, 705, 1901; Rolloff, *ib.*, **13**, 341, 1894; Jakowkin, *ib.*, **20**, 19, 1896; Hendrixson, *Zeit. f. anorg. Chem.*, **13**, 73, 1897; Riecke, *Zeit. f. phys. Chem.*, **7**, 108, 1891; H. Fischer, Dissertation, Breslau, 1905.

⁴ Morgan's "Physical Chemistry for Electrical Engineers," pp. 117-118, 1906.

⁵ Nernst, *l. c.*

If, as we must in experimental work, use grams instead of moles, we find, since $C_1 = W_1/M_1$, $C_2 = W_2/M_2$ and $M_1 = nM_2$, that $K = C_1/C_2^n$ can also be written in the form $M_1/M_2^n K = w_1/w_2^n$ where w_1 and w_2 are weights in grams per unit of volume. In other words so long as at all dilutions M_1/M_2^n is a constant we can use w_1/w_2^n in place of C_1/C_2^n .

Alcohol and acetic acid which as has been seen in the earlier part of this paper show abnormal results in $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, according to the freezing point, have been treated by this method, as have also various solutions of alcohol and benzene mentioned above, with the following results:

XXXI. Distribution of acetic acid between water and ether

C_w grams acetic acid per cc.	C_E grams acetic acid per cc.	$\frac{C_w}{C_E}$
0.0320	0.0169	1.89
0.1483	0.0835	1.77
0.1963	0.0936	2.09
0.2552	0.1208	2.10
0.3458	0.1849	1.87

Average 1.94

XXXII. Distribution of acetic acid between fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and ether.

C Acetic acid in 100 grams $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ before distribution.	$C_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}$	C_E	$K = \frac{C_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}}{C_E}$
4.74	0.0124	0.0175	0.708
7.89	0.0216	0.0285	0.757
9.48	0.0249	0.0358	0.696
22.75	0.0518	0.0767	0.679
37.92	0.0933	0.1229	0.758
63.18	0.1298	0.1940	0.668

Average 0.716

XXXIII. Distribution of acetic acid between ether and fused $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$.

C.	$\text{C}_{\text{LiNO}_3 \cdot 3\text{H}_2\text{O}}$	C_E	$\frac{\text{C}_{\text{LiNO}_3 \cdot 3\text{H}_2\text{O}}}{\text{C}_\text{E}}$
2.349	0.0092	0.0072	1.26
5.872	0.0216	0.0194	1.11
7.075	0.0261	0.0249	1.05
16.442	0.0533	0.0508	1.05
28.300	0.0869	0.0869	1.00
Average			1.09

XXXIV. Distribution of alcohol between water and ether.

C. Approximate weight of alcohol in 100 grams of water before distribution.	C_w . Grams of alcohol in 25 cc. after distribution.	C_E . Grams of alcohol in 25 cc. after distribution.	$\frac{\text{C}_w}{\text{C}_\text{E}}$
2.4	0.145	0.205	0.707
8.0	0.363	0.856	0.583
16.0	0.678	1.042	0.652
20.0	0.820	1.450	0.570
20.0	0.862	1.402	0.611
40.0	1.275	2.372	0.538
Average			0.610

XXXV. Distribution of ethyl alcohol between fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and ether.

C.	$\text{C}_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}$	C_E	$\frac{\text{C}_{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}}{\text{C}_\text{E}}$
1.6	0.0488	0.0484	1.10
5.32	0.3125	0.3087	1.01
8.33	0.3125	0.2625	1.18
10.64	0.4850	0.4150	1.17
16.66	0.5787	0.4487	1.28
36.00	1.2250	0.9670	1.27
Average			1.16

XXXVI. Distribution of ethyl alcohol between fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and benzene.

C.	$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.	C_B .	$\frac{\text{CaCl}_2 \cdot 6\text{H}_2\text{O}}{\text{C}_B}$
50	1.803	0.236	7.59
80	2.853	0.378	7.53

XXXVII. Distribution of ethyl alcohol between water and benzene.

C.	C_w .	C_B .	$\frac{\text{C}_w}{\text{C}_B}$.
8.0	0.500	0.481	1.038
16.0	0.854	0.866	0.986
40.0	1.682	1.967	0.860
80.0	2.420	3.276	0.740

Average 0.906

Equal volumes of the two solvents were used throughout. The acetic acid was titrated with standard base, using phenolphthalein as indicator.

The content of alcohol in the two layers was found by the method of Thorpe and Holmes.¹ 25 cc of the layer were removed and placed in a separating funnel, diluted 100 cc with water, saturated with sodium chloride and 40 cc of petroleum ether added. After shaking for five minutes the layers were allowed to separate and the lower one withdrawn for distillation. The layer of petroleum ether was washed several times with saturated salt solution and the washings added to the main portion. The latter was next distilled through a Hopkins head and condenser into a 50 cc flask, protected against evaporation by means of an adapter. This flask, after distillation had continued so that one-fourth of the original solution had distilled over, was filled to the mark with distilled water. To determine the amount of alcohol in grams in this distillate the specific gravity of the latter was determined by use of a Sprengel-Ostwald pycnometer and from the specific gravity, by means

¹ *Trans. Chem. Soc.*, **83**, 314, 1903.

of the conversion table of Morley,¹ the per cent of alcohol by weight was determined. This weight was the amount of alcohol present in the original 25 cc.

IX. DISCUSSION OF DISTRIBUTION RESULTS.

Before using ether as the second solvent it was necessary to find the molecular weights of alcohol and acetic acid, when dissolved in it. As these cannot be found by aid of the freezing point and as solute as well as solvent distills when heated, the boiling point cannot be used conveniently, there is no direct method which is applicable. The method, to a certain extent indirect, which was used for the purpose was also based upon the coefficient of distribution. The molecular weights of ethyl alcohol and acetic acid in water have been determined up to high concentrations² and increase but slightly with increased concentration, *i. e.*, have a small heat of concentration (see above), assuming the gas laws to hold rigidly. Solutions of ethyl alcohol and acetic acid were shaken with an equal volume of ether and gave (see Tables XXXIV and XXXI) a practically constant coefficient of distribution, within the experimental error. It will be observed comparing these with Tables XXXII and XXXIII, that acetic acid and alcohol between fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, or fused $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and ether, show the same constancy of coefficient. This proves, indirectly, then that acetic acid has practically the same molecular weight in ether as in water (which is nearly constant according to freezing point determinations) and this molecular weight is the same, according to distribution experiments, as that in fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, notwithstanding that the freezing point in this leads to the abnormal molecular weights given above. The same inferences are to be drawn from the results for alcohol in fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and for acetic acid in the latter. Further, the coefficient of distribution shows that the molecular weight of alcohol in benzene cannot be very variable, although Beckman's³ results by freezing point lead to absurd values.

¹ *Jour. Am. Chem. Soc.*, 26, 1185, 1904.

² Jones and Murray, *Am. Chem. Jour.*, 30, 205, 1903.

³ *Loc. cit.*

Since granting that the gas laws hold in solutions, the heat of concentration is one of the factors leading to abnormal results for molecular weight by the freezing point, or any other method related in the same way to osmotic pressure it is to be expected that a method not so related in the same way to osmotic pressure would be unaffected by the heat of concentration. It is very evident by the derivation given above for the coefficient of distribution, from the law of mass action, and it can readily be shown for the other derivations, that the heat of concentration or dilution has no influence upon the coefficient of distribution and consequently the results obtained above were but to be expected.

In the case of the system acetic acid, ether, and water, a very large quantity of acetic acid will cause but one layer to be formed. At first glance it would seem that this might affect the distribution, but a moment's thought will show that it would only do so under certain conditions, which are not encountered here. When the quantity of acetic acid is large and is successively increased, each layer, instead of being the solution of pure solvent and substance, will contain an ever-increasing amount of the other solvent. So long as the substance has the same molecular weight in both, however, the mixture of solvents will still give an unchanged molecular weight and the coefficient of distribution will remain constant. When one solvent leads to a molecular weight equal to twice that in the other on the contrary, such a variation in the nature of the layers will cause inconstancy in the relation, for each solvent in the other will change the molecular weight in that, until finally each layer will lead to the same value, the mean of the two, and the ratio C_1/C_2 will become constant, instead of C_1^2/C_2 . To this influence undoubtedly is to be attributed the peculiar values of the coefficient of acetic acid between water and various other liquids¹. Only in the case that the other solvent leads to the same molecular weight as does water, *i. e.*, amyl alcohol and ether for acetic acid, does the coefficient of distribution of acetic acid between water and the other solvent in any form remain constant. This effect naturally is only observed in those cases where the substance,

¹ Herz and Lowry, *l. c.* Fisher, *l. c.*

being distributed, is a liquid which will ultimately cause one phase to be formed from the two.

IX. CONCLUSIONS.

The results of this investigation may be summarized as follows:

1. Fused salts, containing water of crystallization may be used as solvents for the freezing point method and give values similar to those determined in water, except that the ionization of the substances added when it has an ion in common with the solvent is decreased or practically excluded.

2. The freezing point constants, assuming the gas laws to hold and neglecting the heats of concentration, for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ are respectively 45.0 (freezing point = $29^\circ.48$); 26.0 (freezing point = $29^\circ.88$); and 38.7 (freezing point = $19^\circ.92$).

3. The latent heat of fusion of $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ as calculated from its freezing point constant under the above conditions, *i. e.*, w in $K = \frac{0.02 T^2}{w}$, is equal to 70.6 cal per gram at its freezing point $29^\circ.88$.

4. The apparent molecular weight of acetic acid in fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ is not affected by the addition of an equimolecular weight of formic acid, the freezing points of the mixture being practically the mean of the values found for the two separately.

5. A formula is suggested, though not as yet applied, to show the effect of the heat of solution upon the freezing point depression. Assuming that the gas laws hold in solution, we have $\Delta'_x = \frac{T(2xT + Q)}{100w - Q}$, where Δ'_x is the corrected depression due to the solu-

tion of x moles per 100 grams of solvent, T is the freezing temperature, w the latent heat of fusion, and Q the heat involved when a solution which contains x moles per 100 grams is concentrated by the removal of 100 grams of solvent, Q is positive when heat is evolved as the substance dissolves, and negative when heat is absorbed by the solution of the substance.

6. This formula can also be used for the boiling point method

still assuming the gas laws to hold, if the proper values of x , T , Q and W are substituted.

7. The molecular weights of alcohol in ether and of acetic acid in ether, according to the coefficient of distribution, are the same as in water.

8. The coefficient of distribution shows practically unchanging molecular weights for acetic acid alcohol in fused $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and in fused $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, and for alcohol in benzene, although the uncorrected freezing points of such solutions lead to increasingly abnormal and absurd values.

9. The coefficient of distribution is independent of the heat of solution and probably tends to decrease any variation due to the non-holding of the gas laws in solution.

10. It is suggested that the abnormal coefficient of distribution for acetic acid between water and various other solvents (all of which show varying polymerization) which have been observed by others are caused by the increase of solubility of each layer in the other, due to the presence of the third liquid and the consequent changing in each of the molecular weight. This effect is not noticed in case the solvent leads to the same molecular weight of acetic acid as does water (ether and amyl alcohol).

BIOGRAPHICAL.

H. K. Benson entered Franklin and Marshall College in 1896 and was granted the degree of Bachelor of Arts in 1899 and of Master of Arts in 1902. During 1903-1904 he pursued graduate work in Johns Hopkins University and during the following two years was an assistant Professor of Chemistry in the University of Washington. In 1906 he was granted a leave of absence to continue graduate work in Columbia University. In the latter place he has been, during the past year, University Fellow in chemistry.

